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# Effect of high temperature heat treatment in vacuum on microstructure and bending properties of $SiC_f/SiC$ composites prepared by CVI

Hiroshi Araki [a,*], Hiroshi Suzuki [a], Wen Yang [a], Shinji Sato [b], Tetsuji Noda [a]

[a] *National Research Institute for Metals, 1-2-1, Sengen, Tsukuba, Ibaraki 305, Japan*
[b] *Fukushima National College of Technology, 30 Nagao, Taira-Kamiarakawa, Iwaki, Fukushima 970, Japan*

**Abstract**

Thermal stabilities of $SiC_f/SiC$ composites prepared with chemical vapor infiltration have been examined. Three types of SiC fibers of commercial grade Nicalon, Hi-Nicalon and stoichiometric Hi-Nicalon Type-S with oxygen concentrations of respectively 11.7%, 0.5% and 0.2% were used as preforms. After heat treatment at 1273–2273 K in vacuum, changes in oxygen content of the composites were measured. Bending properties such as flexural strength and fracture toughness were also examined at room temperature. Deoxidation was clearly observed for the commercial grade Nicalon $SiC_f/SiC$ composite ($SiC_f(CG)/SiC$) at temperatures above around 1700 K. Furthermore, decomposition of fibers completely occurred above 1973 K for $SiC_f(CG)/SiC$. A slight degradation was also observed for Hi-Nicalon $SiC_f/SiC$ composite. On the other hand, Hi-Nicalon Type-S $SiC_f/SiC$ did not show an apparent degradation even after heat treating at 2200 K. The decomposition of the commercial grade Nicalon SiC fibers can be mainly explained by the sublimation of SiO which is formed according to the reaction $SiC_xO_y \rightarrow SiO+SiC$.

## 1. Introduction

$SiC_f/SiC$ composite is considered as one of the candidates for first wall and blanket structural materials of fusion reactors because of its high temperature strength, improved fracture toughness and low induced activity under the irradiation of fusion neutrons. Among several processes for ceramic composites, chemical vapor infiltration (CVI) has an advantage in high purity [1,2], minimizing damage to fibers and making near-net shape products. In CVI process, Nicalon SiC is generally used for the preform because of a continuous fiber with high flexibility. However, the instability of the fiber against irradiation and high temperature has been pointed out [3–5] since Nicalon fiber which is commercially available contains a high concentration of oxygen.

In the present paper, the microstructure and mechanical properties of CVI $SiC_f/SiC$ composites prepared with SiC fibers with different chemical compositions and the stabilities at high temperatures in vacuum have been studied.

## 2. Experimental

Nicalon commercial grade fiber ($SiC_f(CG)$), Hi-Nicalon SiC fiber ($SiC_f(Hi)$), and Hi-Nicalon Type-S fiber ($SiC_f(S)$) were used as preforms. The chemical compositions are $Si_{0.374}C_{0.490}O_{0.136}$ for $SiC_f(CG)$, $Si_{0.416}C_{0.578}O_{0.006}$ for $SiC_f(Hi)$ and $Si_{0.487}C_{0.511}O_{0.002}$ for $SiC_f(S)$. These chemical formula indicate that $SiC_f(CG)$, $SiC_f(Hi)$ and $SiC_f(S)$ contain oxygen of 11.7, 0.5 and 0.2 mass%, respectively. $SiC_f(S)$ has nearly stoichiometric composition of SiC. The uni-directional (UD) fiber preforms with a disk shape, 40 mm $\phi \times 3$ mm, were infiltrated with SiC using thermal decomposition of trichloro-ethyl-silane (ETS). The ratio of fiber to matrix was around

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[*] Corresponding author. Tel.: +81 298 59 2848; fax: +81 298 592801; e-mail: araki@nrim.go.jp.

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1. The reactant having a purity better than 99 vol% was carried by $H_2$ gas with a volume ratio of 1/150 to $H_2$. The temperature and the pressure at the downstream side of the specimen were kept at 1273 K and 17 kPa, respectively. Composites formed were identified with X-ray diffraction. Bending specimen with or without a notch had a rectangular form with 3 mm in width, 30 mm in length and 2.5 mm in thickness. The notch length was a half length of the thickness. The thermal stability experiment was performed at 1273–2273 K in a vacuum of $2 \times 10^{-4}$ Pa. After heat treatments, bending tests were conducted so that the bending direction crossed the laminated preform structure with a cross-head speed of 0.0083 mm/s. The fractured surface was observed by SEM and changes in oxygen content of specimens by the heat treatment were measured by chemical analysis. The structure change with the heat treatment of fibers themselves in a vacuum was also examined with X-ray diffraction analysis.

## 3. Results

### 3.1. Microstructures of the composites

Fig. 1 shows the cross sectional microstructures of the $SiC_f$(CG)/SiC and $SiC_f$(Hi)/SiC as received and after heat treatment in vacuum. The present samples had an average porosity of 5–10%. Morphology changed with increasing temperature. The interface between fiber and matrix was roughened by the heating; especially the $SiC_f$(CG) changed in shape at high temperatures and completely lost the fibrous form at 2273 K, while $SiC_f$(Hi) kept its structure in the present temperature range though the surface of fibers roughened as seen in this figure.

Fig. 2 shows the microstructures of $SiC_f$(S)/SiC as received and after the heat treatment. No change in microstructure was observed for the $SiC_f$(S)/SiC composite even after heat treating at high temperatures up to about 2200 K.

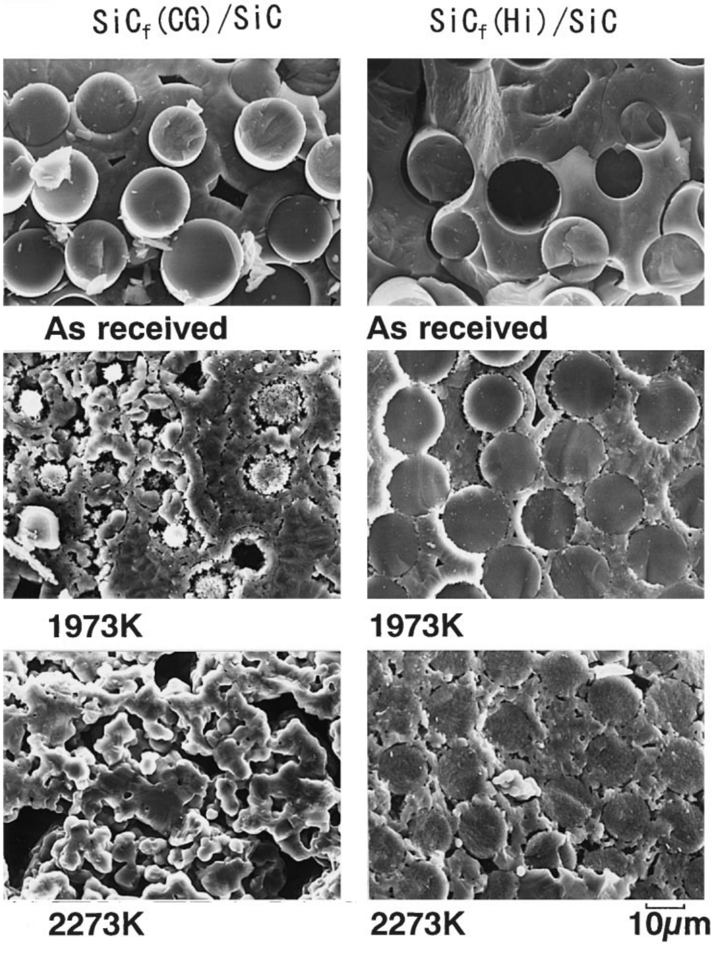

Fig. 1. Microstructures of the $SiC_f$(CG)/SiC and $SiC_f$(Hi)/SiC composites as received and after heat treatment for 3.6 ks in vacuum.

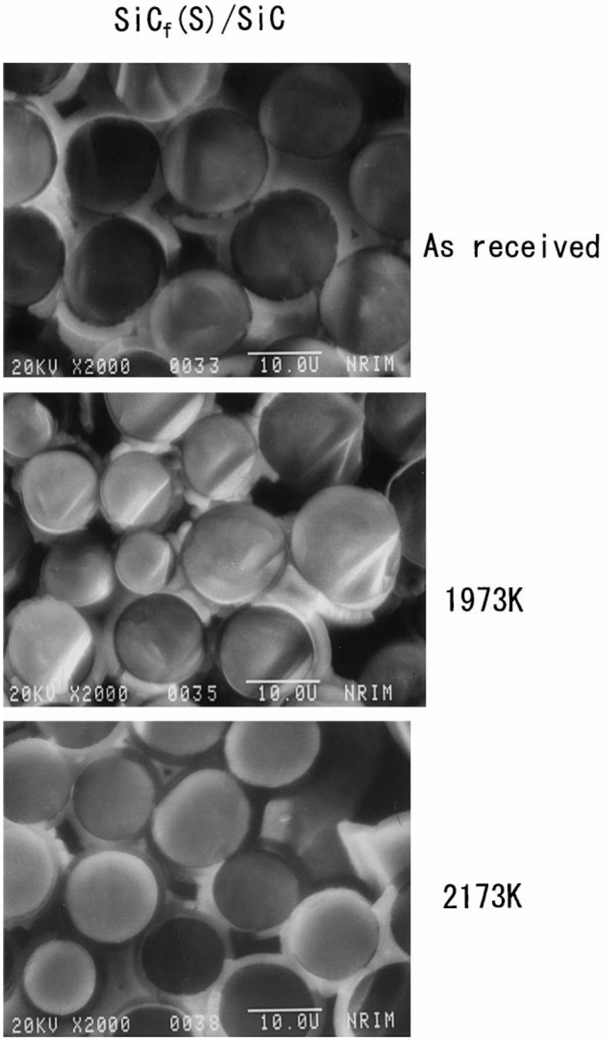

Fig. 2. Microstructures of the SiC$_f$(S)/SiC composite as received and after heat treatment for 3.6 ks in vacuum.

### *3.2. Change in oxygen content of the composites heat treated in vacuum*

Fig. 3 shows the plot of oxygen content of the composites after the heat treatment for 3.6 ks at various temperatures. The oxygen concentrations as received were 5.6% for the SiC$_f$(CG)/SiC and about 1% for the SiC$_f$(Hi)/SiC and SiC$_f$(S)/SiC. The oxygen content measured was an average value in the composite. Some amount of oxygen was considered to be incorporated into the composite during the CVI process since the composites contains pores. Oxygen content decreased with the increasing temperature. The sharp decrease in oxygen concentration is observed above around 1700 K where the SiC$_f$(CG) begins to decompose as expected in Fig. 1. On the other hand, the SiC$_f$(Hi)/SiC and SiC$_f$(S)/SiC do not indicate such abrupt deoxidation because of their low oxygen content. The results of measurements of oxygen content with time at various temperatures indicated that the deoxidation of SiC$_f$(CG)/SiC slightly occurred at 1573 K though the clear deoxidation was observed above around 1773 K.

The weight loss of the composites during the heat treatment was also measured. The results are shown as a function of heat treatment temperature in Fig. 4. The specimens were heat treated for 3.6 ks. The composites lost their weight with increasing temperature. Especially large weight loss was observed for the SiC$_f$(CG)/SiC composite with increasing temperature. The weight loss of the SiC$_f$(Hi)/SiC and the SiC$_f$(S)/SiC is considered mainly due to sublimation of SiC because of low oxygen content.

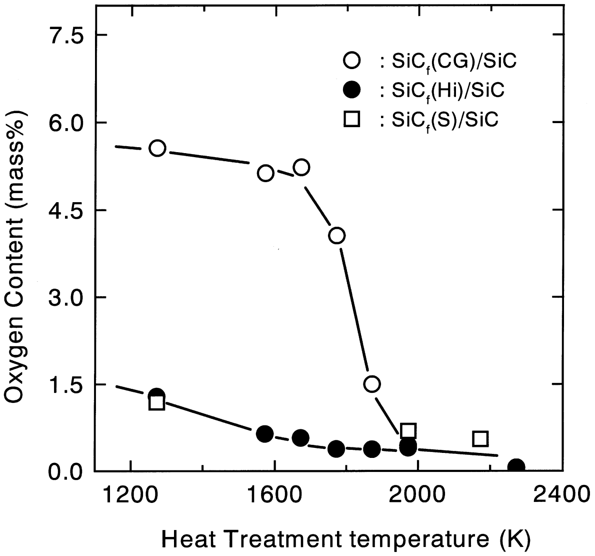

Fig. 3. Change in oxygen content of the composites with heat treatment temperature.

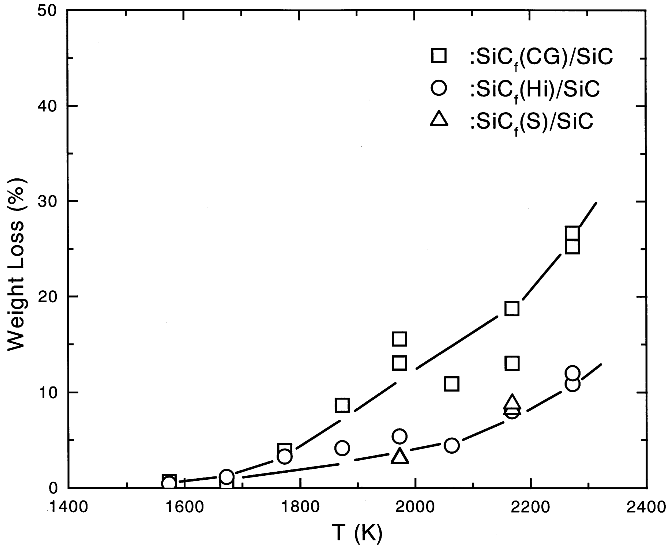

Fig. 4. Weight loss of the composites after heat treatment for 3.6 ks in vacuum.

### *3.3. Bending properties*

Fig. 5 shows the fracture strength as a function of heat treatment temperature. The specimens were heated for 3.6 ks in vacuum. There is a tendency that the strength is in order of SiC$_f$(S)/SiC > SiC$_f$(Hi)/SiC $\geqslant$ SiC$_f$(CG)/SiC though the data are rather scattered. The strength abruptly decreased with temperature above around 1700 K for both SiC$_f$(CG)/SiC and SiC$_f$(Hi)/SiC. On the other hand, the SiC$_f$(S)/SiC kept the strength even at around 2000 K.

Shear fracture due to the strain tolerance by bridging and pull-out of fibers was observed for the SiC$_f$(Hi)/SiC even after heat treating at 2273 K while the SiC$_f$(CG)/SiC showed a sharp fracture after the heat treatment at 2273 K where the SiC fiber lost a fibrous structure as seen in Fig. 2. The fracture appearance of SiC$_f$(S)/SiC was almost the same as that of the SiC$_f$(Hi)/SiC and the specimens heat treated even at 2173 K could not be completely fractured because the fibers did not deteriorate.

The fracture toughness of both SiC$_f$(CG)/SiC and SiC$_f$(Hi)/SiC composites as received was 10–27 MPa

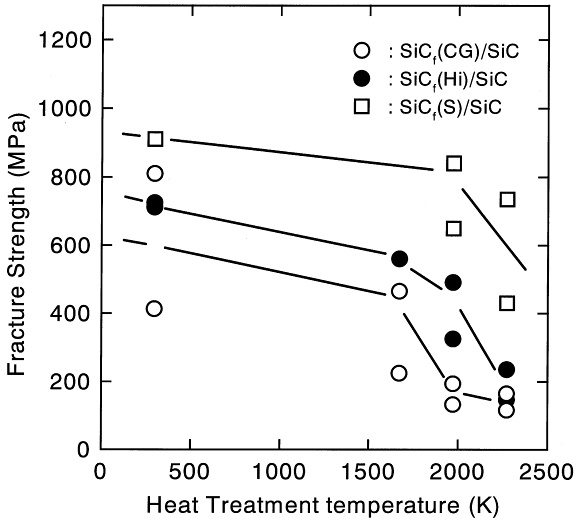

Fig. 5. Relations between fracture strength of the composites and heat treatment temperature.

$m^{1/2}$ which is about one order of magnitude higher than that of monolithic SiC. The fracture toughness of the SiC$_f$(CG)/SiC decreased with increasing the temperature and was reduced to around 1 MPa $m^{1/2}$ after heat treatment at 2273 K. This can be explained by the change in morphology of the composite after heat treating above 1973 K as described above. The toughness of SiC$_f$(Hi)/SiC also decreased with temperature. However it kept around 5 Mpa $m^{1/2}$ even at 2273 K. The toughness of SiC$_f$(S)/SiC is not expected to be severely reduced by the heat treatment judging from the high strength kept even at 2200 K as shown in Fig. 5 though the toughness was not measured in the present study.

## 4. Discussion

As it has been described in the previous chapter, there is almost no difference in microstructure and bending properties between SiC$_f$/SiC composites prepared with SiC fibers with a different chemical composition. However, deoxidation after heat treatment above 1700 K in vacuum, leading to the degradation of mechanical properties of the SiC composites, was observed especially for the SiC$_f$(CG)/SiC composite. When the composites are heat treated at elevated temperatures above 1573 K in vacuum, the following reactions are assumed to occur.

Since the SiC$_f$(CG) has a composition like $SiC_xO_y$, the SiC fiber in the SiC$_f$(CG)/SiC decomposes as:

$$SiC_xO_y \rightarrow SiO\ (\text{sublimation}) + SiC \tag{1}$$

or

$$SiC_xO_y \rightarrow SiC + CO\ (\text{gas}) \tag{2}$$

and SiC of the matrix partially sublimates as

$$SiC \rightarrow SiC\ (\text{sublimation}). \tag{3}$$

In the case of SiC$_f$(Hi),

$$SiC_{1+x} + \text{trace O in fiber} \rightarrow SiC + CO\ (\text{gas}) \tag{4}$$

in addition to reaction (3). For SiC$_f$(S), only SiC is considered to sublimate in vacuum at high temperatures according to Eq. (3).

Fig. 6 shows the comparison in oxygen concentration between measured and estimated values for the SiC$_f$(CG)/SiC after the heat treatment. The dotted line in this figure was estimated from the weight loss of the SiC$_f$(CG)/SiC composite assuming that it loses both Si and O as a form of SiO from the fibers in addition to the sublimation of SiC, and the SiC$_f$(S)/SiC loses its weight by only SiC sublimation. Fairly good coincidence is observed between these two values. That is, the deoxidation of the composite during the heat treatment in the vacuum is considered mainly due to the sublimation of SiO resulting from the decomposition of SiC fiber as expressed in Eq. (1).

With respect to mechanical properties, both SiC$_f$(CG)/SiC and SiC$_f$(Hi)/SiC showed decrease in fracture strength with increasing temperature above 1700 K. Then the structures of the fibers after heat treatment were more precisely examined with X-ray diffraction analysis. The fibers heat treated for 3.6 ks at various temperatures in vacuum were ground to powders. The same amount of powder for each fiber was analyzed by X-ray diffraction. All fibers as received indicated typical diffraction patterns of β-SiC though

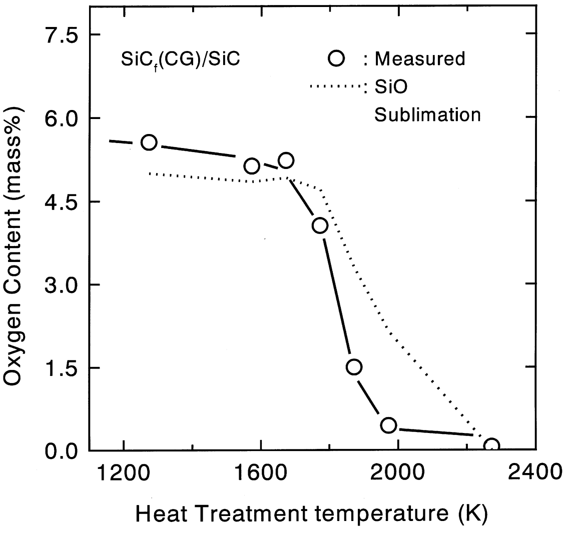

Fig. 6. Comparison in oxygen concentration change for the SiC$_f$(CG)/SiC between measured and calculated values assuming the sublimation of SiO.

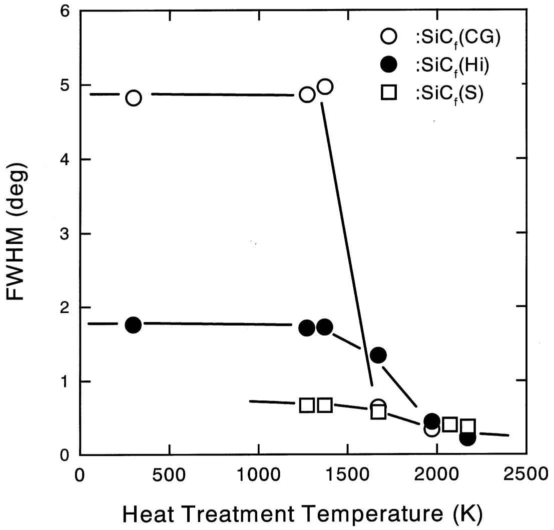

Fig. 7. FWHM of (1 1 1) diffraction peak of β-SiC for SiC fibers as a function of heat treatment temperature.

SiC$_f$(CG) showed a broad peak. That is, all Nicalon fibers are essentially based on β-SiC structure.

Fig. 7 shows the full width at half maximum (FWHM) of (1 1 1) peak of β-SiC for fibers as a function of heat treatment temperature. The FWHM decreases with increasing temperature for both SiC$_f$(CG) and SiC$_f$(Hi) fibers. Especially large reduction in FWHM occurred for the SiC$_f$(CG), which indicated that SiC crystallite size of fibers increased with the deoxidation reaction of Eq. (1) ignoring the strain in the crystals [6]. The SiC$_f$(Hi) with excess carbon also showed the decrease of FWHM above 1700 K. On the other hand, SiC$_f$(S) with a stoichiometric composition hardly shows a change of FWHM even after heat treatment at 2200 K. The deterioration of the composites at high temperatures in a vacuum is therefore considered to be mainly caused by the deoxidation and crystallite growth of SiC fibers.

## 5. Conclusion

SiC$_f$/SiC composites were prepared from Nicalon CG, Hi-Nicalon, and Hi-Nicalon Type-S SiC fibers using CVI process. Thermal stabilities of the composites at 1273–2273 K in vacuum were examined.

Conclusions are:

1. Remarkable weight loss and deoxidation occurred above 1700 K for the SiC$_f$(CG)/SiC composite. Moreover, SiC$_f$(CG) fiber with a high oxygen content decomposed above 1973 K. A slight deoxidation occurred for the SiC$_f$(Hi)/SiC while fibrous shape of the SiC$_f$(Hi) was kept even at 2273 K. No apparent deterioration of SiC$_f$(S) fibers was observed for SiC$_f$(S)/SiC composites after heat treatment at temperatures up to 2200 K.
2. Both fracture strength and fracture toughness decreased with increasing heat treatment temperature for SiC$_f$(CG)/SiC and SiC$_f$(Hi)/SiC composites, while SiC$_f$(S)/SiC indicated the highest strength and lowest reduction in strength with increasing temperature.
3. Deoxidation of the composite can be mainly explained by the sublimation of SiO resulted from the decomposition of SiC fiber for the SiC$_f$(CG)/SiC composite.
4. SiC$_f$/SiC composites prepared with stoichiometric SiC fibers showed a high strength and thermal stability in vacuum at temperatures up to 2200 K.

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